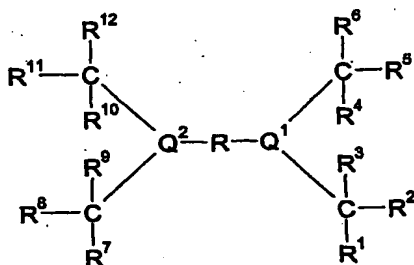


CLAIMS

1. A process for the hydroformylation of ethylenically unsaturated compounds, which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of a catalyst system, the catalyst system obtainable by combining:

- a) a Group VIII metal compound; and
- b) a bidentate phosphine of general formula (Ia)

(Ia)



wherein:

R is a bridging group;

R<sup>1</sup> to R<sup>12</sup> each independently represent hydrogen, lower alkyl, aryl or Het, preferably, lower alkyl, aryl or Het;

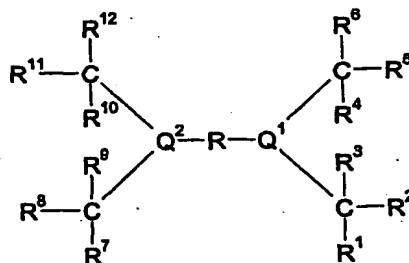
Q<sup>1</sup> and Q<sup>2</sup> each independently represent phosphorus, arsenic or antimony and in the latter two cases references to phosphine or phosphorus above are amended accordingly,

the process characterised in that a chlorine moiety is present in at least said Group VIII metal compound.

2. A process for the hydroformylation of ethylenically unsaturated compounds, which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of a catalyst system and a solvent, the catalyst system obtainable by combining:

- a) a metal of Group VIII or a compound thereof; and
- b) a bidentate phosphine of general formula (Ia)

(Ia)



wherein:

R is a bridging group;

R<sup>1</sup> to R<sup>12</sup> each independently represent hydrogen, lower alkyl, aryl or Het, preferably, lower alkyl, aryl or Het;

Q<sup>1</sup> and Q<sup>2</sup> each independently represent phosphorus, arsenic or antimony and in the latter two cases references to phosphine or phosphorus above are amended accordingly,

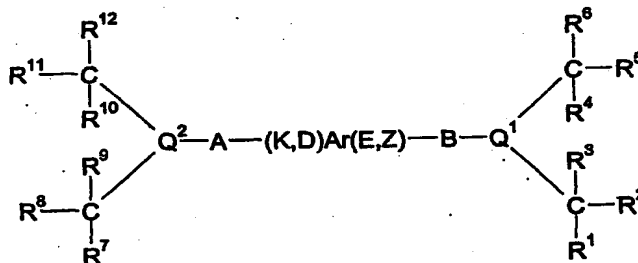
the process characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent.

3. The process as claimed in claim 2, wherein a chlorine moiety is present in both said Group VIII metal compound and said solvent.
4. The process as claimed in any of claims 1 to 3, wherein  $R^1$  to  $R^{12}$  each independently represent  $C_1$  to  $C_6$  alkyl,  $C_1$  to  $C_6$  alkyl phenyl or phenyl.
5. The process as claimed in claim 4, wherein  $R^1$  to  $R^{12}$  each independently represent methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.
6. The process as claimed in any preceding claim, wherein  $R^1$ ,  $R^4$ ,  $R^7$  and  $R^{10}$  each independently represent the same  $C_1$ - $C_6$  alkyl;  $R^2$ ,  $R^5$ ,  $R^8$  and  $R^{11}$ , each independently represent the same  $C_1$ - $C_6$  alkyl; and  $R^3$ ,  $R^6$ ,  $R^9$  and  $R^{12}$ , each independently represent the same  $C_1$ - $C_6$  alkyl.
7. The process as claimed in any preceding claim, wherein  $R^1$  to  $R^{12}$  each represents the same  $C_1$ - $C_6$  alkyl group.
8. The process as claimed in claim 7, wherein the said  $C_1$ - $C_6$  alkyl group is non-substituted and selected from the list comprising: methyl, ethyl, n-propyl, iso-

propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.

9. The process as claimed in claim 8, wherein the said C<sub>1-6</sub> alkyl group is methyl.
10. The process as claimed in any preceding claim, wherein Q<sup>1</sup> and Q<sup>2</sup> represents phosphorus.
11. The process as claimed in any one of claims 1 to 3 wherein R is defined as -A-(K,D)Ar(E,Z)-B- and the bidentate phosphine is of general formula (I)

(I)



wherein:

Ar is a bridging group comprising an optionally substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

A and B each independently represent lower alkylene;

K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR<sup>19</sup>, OC(O)R<sup>20</sup>,

$C(O)R^{21}$ ,  $C(O)OR^{22}$ ,  $NR^{23}R^{24}$ ,  $C(O)NR^{25}R^{26}$ ,  $C(S)R^{25}R^{26}$ ,  $SR^{27}$ ,  $C(O)SR^{27}$ , or  $-J-Q^2(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$  where  $J$  represents lower alkylene; or two adjacent groups selected from K, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro,  $OR^{19}$ ,  $OC(O)R^{20}$ ,  $C(O)R^{21}$ ,  $C(O)OR^{22}$ ,  $NR^{23}R^{24}$ ,  $C(O)NR^{25}R^{26}$ ,  $C(S)R^{25}R^{26}$ ,  $SR^{27}$  or  $C(O)SR^{27}$ ;

$R^1$  to  $R^{18}$  each independently represent lower alkyl, aryl, or Het;

$R^{19}$  to  $R^{27}$  each independently represent hydrogen, lower alkyl, aryl or Het;

$Q^1$ ,  $Q^2$  and  $Q^3$  (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly.

12. The process as claimed in claim 11, wherein  $R^1$  to  $R^{18}$  each independently represent  $C_1$  to  $C_6$  alkyl,  $C_1$  to  $C_6$  alkyl phenyl or phenyl.
13. The process as claimed in claim 12, wherein  $R^1$  to  $R^{18}$  each independently represent methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.
14. The process as claimed in any of claims 11 to 13 wherein  $R^1$ ,  $R^4$ ,  $R^7$ ,  $R^{10}$ ,  $R^{13}$  and  $R^{16}$  each independently

represent the same C<sub>1</sub>-C<sub>6</sub> alkyl; R<sup>2</sup>, R<sup>5</sup>, R<sup>8</sup>, R<sup>11</sup>, R<sup>14</sup> and R<sup>17</sup> each independently represent the same C<sub>1-6</sub> alkyl; and R<sup>3</sup>, R<sup>6</sup>, R<sup>9</sup>, R<sup>12</sup>, R<sup>15</sup> and R<sup>18</sup> each independently represent the same C<sub>1-6</sub> alkyl.

15. The process as claimed in any of claims 11 to 14, wherein R<sup>1</sup> to R<sup>18</sup> each represents the same C<sub>1</sub>-C<sub>6</sub> alkyl group.
16. The process as claimed in claim 15, wherein the said C<sub>1-6</sub> alkyl group is non-substituted and selected from the list comprising: methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.
17. The process as claimed in claim 16, wherein the said C<sub>1-6</sub> alkyl group is methyl.
18. The process as claimed in any of claims 11 to 17, wherein Q<sup>1</sup>, Q<sup>2</sup> and Q<sup>3</sup> (when present) represents phosphorus.
19. The process as claimed in any of claims 11 to 18, wherein A, B and J (when present) each independently represent C<sub>1</sub> to C<sub>6</sub> alkylene.
20. The process as claimed in claim 19, wherein each of A, B and J (when present) represent -CH<sub>2</sub>-.
21. The process as claimed in any of claims 11 to 20, wherein K, D, E and Z each represent hydrogen, phenyl, C<sub>1</sub>-C<sub>6</sub> alkylphenyl or C<sub>1</sub>-C<sub>6</sub> alkyl.

22. The process as claimed in claim 21, wherein K, D, E and Z each represent hydrogen.

23. The process as claimed in claim 11 wherein in formula (I):

A and B each independently represent unsubstituted C<sub>1</sub> to C<sub>6</sub> alkylene;

K, D, Z and E each independently represent hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl, phenyl, C<sub>1</sub>-C<sub>6</sub> alkylphenyl or -J-Q<sup>3</sup>(CR<sup>13</sup>(R<sup>14</sup>)(R<sup>15</sup>))CR<sup>16</sup>(R<sup>17</sup>)(R<sup>18</sup>) where J represents unsubstituted C<sub>1</sub> to C<sub>6</sub> alkylene; or two of K, D, Z and E together with the carbon atoms of the aryl ring to which they are attached form a phenyl ring which is optionally substituted by one or more substituents selected from lower alkyl, phenyl or lower alkylphenyl;

R<sup>1</sup> to R<sup>18</sup> each independently represent C<sub>1</sub> to C<sub>6</sub> alkyl, phenyl or C<sub>1</sub> to C<sub>6</sub> alkylphenyl.

24. The process as claimed in claim 11 wherein in formula (I):

A and B both represent -CH<sub>2</sub>- or C<sub>2</sub>H<sub>4</sub>;

K, D, Z and E each independently represent hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl, phenyl or C<sub>1</sub>-C<sub>6</sub> alkyl or -J-Q<sup>3</sup>(CR<sup>13</sup>(R<sup>14</sup>)(R<sup>15</sup>))CR<sup>16</sup>(R<sup>17</sup>)(R<sup>18</sup>) where J is the same as A; or two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form an unsubstituted phenyl ring;

$R^1$  to  $R^{18}$  each independently represent  $C_1$  to  $C_6$  alkyl;

25. The process as claimed in claim 24, wherein A and B both represent  $-CH_2-$ .

26. The process as claimed in claim 11, wherein in formula (I):

each  $R^1$  to  $R^{12}$  is the same and represents methyl;  
A and B are the same and represent  $-CH_2-$ ;  
K, D, Z and E are the same and represent hydrogen.

27. The process as claimed in any of claims 11 to 26, wherein the reaction is carried out at a temperature of between  $20^\circ\text{C}$  and  $180^\circ\text{C}$ .

28. The process as claimed in claim 27, wherein the temperature is in the range  $50^\circ\text{C}$  to  $150^\circ\text{C}$ .

29. The process as claimed in any of claims 11 to 28, wherein the reaction is carried out under a partial pressure of carbon monoxide/hydrogen in the range of 1 to 700 bar.

30. The process as claimed in claim 29, wherein the partial pressure is in the range 1 to 300 bar.

31. The process as claimed in any of claims 11 to 30, wherein said ethylenically unsaturated compound has 1 to 3 carbon-carbon double bonds per molecule.



32. The process as claimed in claim 31, wherein said compound has 1 carbon-carbon double bond per molecule.
33. The process as claimed in any of claims 11 to 32, wherein the amount of bidentate compound of formula (I) to unsaturated compound is in the range  $10^{-5}$  to  $10^{-2}$  moles per mole of unsaturated compound.
34. The process as claimed in any of claims 11 to 33, wherein said catalyst system further comprises a support.
35. The process as claimed in any of claims 11 to 34, wherein said bidentate phosphine is selected from the group comprising bis (di-*t*-butyl phosphino)-*o*-xylene; 1,2 bis (diadamantylphosphinomethyl) benzene; 1,2 bis (diadamantylphosphinomethyl) naphthalene; 1,2 bis (di-*t*-pentyl phosphino)-*o*-xylene; and bis 1,2 (di-*t*-butyl phosphino) naphthalene.
36. The process as claimed in any of claims 11 to 35, wherein the mol:mol range of compounds of formula (I) to Group VIII metal is in the range of 1:1 to 3:1.
37. The process as claimed in claim 36, wherein said mol:mol range is in the range of 1:1 to 1.25:1.
38. The process as claimed in any of claims 11 to 37, wherein the Group VIII metal is selected from the group: cobalt, nickel, palladium, rhodium, ruthenium and platinum.

39. The process as claimed in claim 38, wherein said Group VIII metal is rhodium.
40. The process as claimed in any of claims 11 to 39, wherein said chlorine moiety is present in at least said Group VIII metal compound and said compound is selected from the group comprising:  $[\text{RhCl}(\text{CO})_2]_2$ ,  $[\text{RhCl}(\text{Cod})_2]_2$ ,  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ ,  $[\text{RhCl}(\text{Norbornadiene})]_2$ ,  $[\text{RhCl}(\text{Cyclooctene})]_2$ , Chloro(1,5-hexadiene)-rhodium(I)dimer,  $\mu$ -dichlorotetraethylene-dirhodium, (bicyclo[2,2,1]hepta-2-5-diene)chlororhodium(I)dimer.
41. The process as claimed in any of claims 11 to 40, wherein said chlorine moiety is present in at least said Group VIII metal compound and said compound is selected from the group comprising:  $[\text{RhCl}(\text{CO})_2]_2$ ,  $[\text{RhCl}(\text{Cod})_2]_2$  and  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ .
42. The process as claimed in any of claims 11 to 41, wherein said chlorine moiety is present in at least said solvent and said solvent is selected from the group comprising dichloromethane, chlorobenzene, o-dichlorobenzene, m-chlorobenzene, carbon tetrachloride, trichloroethanes, dichloroethanes, chlorofluorocarbons (CFC's), tetrachloroethanes and tetrachloroethene.
43. The process as claimed in claim 42, wherein said solvent is dichloromethane.
44. The process as claimed in any of claims 11 to 43, wherein said ethylenically unsaturated compound has 2 to 20 carbon atoms.

45. The process as claimed in claim 44, wherein said compound has 5 to 15 carbon atoms.
46. The process as claimed in claim 44, wherein said compound has 6 to 12 carbon atoms.
47. The process as claimed in any of claims 11 to 46, wherein said ethylenically unsaturated compound is selected from the group comprising ethene, propene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 3-pentene and branched isomers thereof, 1-hexene and its isomers, 1-heptene and its isomers, 1-octene and its isomers, 1-nonene and its isomers, 1-decene and its isomers, the  $C_{11}$ - $C_{20}$  alkenes and their known isomers, 3-pentenitrile, methyl-3-pentenecarboxylate, 1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-cyclohexadiene, 2,4-heptadiene, and 2-methyl 1,3-butadiene.
48. The process as claimed in any of claims 11 to 47, wherein the said catalyst system further comprises a polymeric dispersant dissolved in a liquid carrier, said polymeric dispersant being capable of stabilising a colloidal suspension of particles of the Group VIII metal or metal compound of the catalyst system within the said liquid carrier.
49. The process as claimed in claim 48, wherein said polymeric dispersant is selected from the list comprising: polyvinylpyrrolidone, polyacrylamide, polyacrylonitrile, polyethylenimine, polyglycine, polyacrylic acid, polymethacrylic acid, poly(3-

hydroxybutyric acid), poly-L-leucine, poly-L-methionine, poly-L-proline, poly-L-serine, poly-L-tyrosine, poly(vinylbenzenesulphonic acid) and poly(vinylsulphonic acid).

50. The process as claimed in claim 49, wherein said polymeric dispersant is selected from the list comprising: polyvinylpyrrolidone and polyacrylic acid.
51. The process as claimed in any of claims 11 to 50, wherein the solvent is formed by one or more of the reactants, products or by-products of the process rather than being a separate entity.
52. A process as claimed in any of claims 11 to 51, wherein Ar is defined as including six-to-ten-membered carbocyclic aromatic groups, such as phenyl and naphthyl, which groups are optionally substituted with, in addition to K, D, E or Z, one or more substituents selected from aryl, lower alkyl, Het, halo, cyano, nitro,  $OR^{19}$ ,  $OC(O)R^{20}$ ,  $C(O)R^{21}$ ,  $C(O)OR^{22}$ ,  $NR^{23}R^{24}$ ,  $C(O)NR^{25}R^{26}$ ,  $SR^{27}$ ,  $C(O)SR^{27}$  or  $C(S)NR^{25}R^{26}$  wherein  $R^{19}$  to  $R^{27}$  each independently represent hydrogen, aryl or lower alkyl.
53. A process as claimed in any preceding claim wherein at least one  $(CR^xR^yR^z)$  group attached to  $Q^1$  and/or  $Q^2$ , i.e.  $CR^1R^2R^3$ ,  $CR^4R^5R^6$ ,  $CR^7R^8R^9$ , or  $CR^{10}R^{11}R^{12}$ , may instead be congressyl or adamantyl, or both groups defined above as  $(CR^xR^yR^z)$  attached to either or both  $Q^1$  and/or  $Q^2$ , may, together with either  $Q^1$  or  $Q^2$  as appropriate, instead form an optionally substituted

2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof.

54. A process as claimed in any of claims 11 to 51 and 53, wherein Ar is a cyclopentadienyl group, and Z may be represented by  $-M(L_1)_n(L_2)_m$  and Z is connected via a metal ligand bond to the cyclopentadienyl group, M represents a Group VIB or VIIIB metal or metal cation thereof; and

$L_1$  represents a cyclopentadienyl, indenyl or aryl group each of which groups are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro,  $OR^{19}$ ,  $OC(O)R^{20}$ ,  $C(O)R^{21}$ ,  $C(O)OR^{22}$ ,  $NR^{23}R^{24}$ ,  $C(O)NR^{25}R^{26}$ ,  $C(S)R^{25}R^{26}$ ,  $SR^{27}$ ,  $C(O)SR^{27}$  or ferrocenyl;

$L_2$  represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO,  $PR^{43}R^{44}R^{45}$  or  $NR^{46}R^{47}R^{48}$ ;

$R^{43}$  to  $R^{48}$  each independently represent hydrogen, lower alkyl, aryl or Het;

$n = 0$  or  $1$ ;

and  $m = 0$  to  $5$ ;

provided that when  $n = 1$  then  $m$  equals  $0$ , and when  $n$  equals  $0$  then  $m$  does not equal  $0$ .

55. A process as claimed in any of claims 1 to 10, wherein R represents an alkylene bridging group, preferably, a lower alkylene.

56. A process for the hydroformylation of ethylenically unsaturated compounds as described hereinbefore with reference to the examples herein.

57. A catalyst system, preferably wherein said system is for use in a process for the hydroformylation of ethylenically unsaturated compounds and which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said system, the catalyst system obtainable by combining:

- a) a Group VIII metal compound as defined in any preceding claim; and
- b) a bidentate phosphine as defined in any preceding claim,

and wherein the catalyst system is characterised in that a chlorine moiety is present in at least said Group VIII metal compound.

58. A hydroformylation reaction catalyst system for the catalysis of ethylenically unsaturated compounds with carbon monoxide and hydrogen in the presence of said system, the catalyst system obtainable by combining:

- a) a Group VIII metal compound as defined in any preceding claim; and

b) a bidentate phosphine as defined in any preceding claim,

and wherein the catalyst system is characterised in that a chlorine moiety is present in at least said Group VIII metal compound.

59. A reaction medium comprising a catalyst system and a solvent, preferably wherein said medium is for use in a process for the hydroformylation of ethylenically unsaturated compounds and which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said system and said solvent, wherein said solvent is as defined in any preceding claim, the catalyst system obtainable by combining:

- a) a metal of Group VIII or a compound thereof as defined in any preceding claim; and
- b) a bidentate phosphine as defined in any preceding claim,

and wherein the reaction medium is characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent, including the possibility of being present in both.

60. A hydroformylation reaction medium, wherein said medium comprises a catalyst system and a solvent, preferably wherein said system is for use in a process for the hydroformylation of ethylenically unsaturated compounds and which process comprises reacting said ethylenically unsaturated compound with carbon monoxide

and hydrogen, in the presence of said system and said solvent, wherein said solvent is as defined in any preceding claim, the catalyst system obtainable by combining:

- a) a metal of Group VIII or a compound thereof as defined in any preceding claim; and
- b) a bidentate phosphine as defined in any preceding claim,

and wherein the reaction medium is characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent, including the possibility of being present in both.

61. The use of a catalyst system as defined in any preceding claim for the hydroformylation of ethylenically unsaturated compounds, said use comprising the step of reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said catalyst system.

62. The use of a reaction medium as defined in any preceding claim for the hydroformylation of ethylenically unsaturated compounds, said use comprising the step of reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said reaction medium.